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# BOTANICAL GAZETTE

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## TOXIC INORGANIC SALTS AND ACIDS AS AFFECTING PLANT GROWTH

(PRELIMINARY COMMUNICATION)

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The economic and industrial phases of the smelter fume and smelter waste problem, especially as related to crop growing in the vicinity of smelters, have been accompanied by a revival of interest in the scientific aspects connected with the physiological effects of the metallic compounds of copper, lead, zinc, and others on plant growth. There have appeared in 1905, 1908, and 1910, respectively, Bulletins 89, 113, and 113 revised, of the Bureau of Chemistry of the United States Department of Agriculture, and all by J. K. HAYWOOD, dealing with the subject of smelter fumes and smelter wastes as related to plant and animal life. HAYWOOD points out in these not only the fact that smelter fumes (largely SO<sub>2</sub>) are very toxic to trees and other plants in the country surrounding the smelters, but in the last two bulletins mentioned devotes some attention to the subject of copper compounds in smelter wastes as affecting the value of irrigation water and soils to be used for crop production. It was this latter fact, together with a desire on our part to obtain further information on the action of manganese in soils and its effects on plants, that led the authors to institute the preliminary experiments which are described below. Before reporting these, however, it is of interest to turn for a moment to a brief review of the results thus far obtained by plant

physiologists and chemists bearing on the subject under considera-

The extreme toxicity of copper to plants under certain conditions has been responsible, it would appear, for some assumptions on the part of investigators as to the similarity in the action of copper in solutions and in soils. Thus Johnson, in his now classic work How crops grow, evidently assumes from the results obtained in solutions that copper is poisonous to plants even in very small quantities. Likewise the work of HEALD<sup>1</sup> and HARTER<sup>2</sup> with plants grown in solutions shows copper to be extremely toxic to plants. The former found, for example, that I part of copper in 404,423 parts of water was deadly to the garden pea (Pisum sativum), and that maize (Zea mays) seedlings are killed by the presence of 1 part of copper in 808,846 parts of water. OSTERHOUT<sup>3</sup> showed how water obtained from copper stills was poisonous to certain of the lower plants when containing merely traces of copper, and HAYWOOD, in the work above mentioned, states that in preliminary work with plants in soils containing copper, the growth of wheat and rye is "interfered with by the presence of 2.1 parts of soluble copper per million parts of earth in one soil, and by 3.5 parts of soluble copper per million parts of earth in another soil."

Some striking results on the effects of copper on plant growth which date back much farther than the last discussed were those obtained at the New York<sup>4</sup> and the Iowa<sup>5</sup> Experiment stations. It is a curious coincidence that both of these investigations were reported in the same year (1892), and they were both the result of the fungicide investigations in which it appeared of interest to ascertain how the continued use of fungicides would affect the soil in its productive capacity. In the New York bulletin, Part I of which is devoted to the subject in question, we find that among peas, wheat, and tomatoes, which formed the test plants, a resistance was noted to as much as 2 per cent and 5 per cent of CuSO<sub>4</sub> of the

<sup>&</sup>lt;sup>1</sup> Bot. Gaz. **22:**125. 1896.

<sup>&</sup>lt;sup>2</sup> Bur. Pl. Ind., U.S. Dept. Agric. Bull. 79. p. 40.

<sup>3</sup> Bot. GAz. 44:272 (footnote). 1907.

<sup>4</sup> N.Y. Exp. Sta. Bull. 41. 1892.

<sup>&</sup>lt;sup>5</sup> Iowa Exp. Sta. Bull. 16. 1892.

dry weight of the soil, and while the soils free from copper gave much larger yields of fruit and vine than did those grown in soils containing copper, it is amazing to note such extreme resistance to large quantities of a poisonous compound on the part of plants as manifested by more or less growth. The author of the paper gives the results only as preliminary and promises a much more thorough review of the investigations later. Twenty years have passed since, however, and we are unable to find any further published data from the New York Experiment Station on that subject. One more note in the paper is of interest, and that is of a contemporary paper by HASELHOFF,6 the conclusions of which are quoted, in which that author states among other things that soluble copper salts are injurious to plants, and that while concentrations up to 5 ppm. are harmless, the presence of 10 ppm. of copper in soil has a marked retarding action. In the Iowa bulletin by PAM-MEL we find that copper solutions had a marked retarding effect on the root development of plants, and that no roots at all developed where the concentration of copper was large. It is unfortunate that PAMMEL does not make mention of the concentrations of copper existing in the various experimental plots in the greenhouse.

So far as the effect of zinc salts on plant growth is concerned, there is but meager information. We have, however, the recent investigations in Germany on the effect of the zinc in galvanized iron cylinders, used for vegetation experiments, on plant growth. From these it would appear that zinc may be distinctly toxic to plant growth.

Experiments with manganese, however, have been very numerous; but their results have been so conflicting as to make more experimental work very desirable. The reader is referred for a more complete bibliography on the effects of manganese in soils on plant growth to a recent publication by W. P. Kelley.<sup>7</sup>

Along with the problems of smelter fumes and smelter wastes, has come the idea of the condensation of the sulphur dioxide and the manufacture of H<sub>2</sub>SO<sub>4</sub>. It has been calculated by COTTRELL and others, however, who have made a careful study of the problems,

<sup>6</sup> Landw. Jahrb. 21:263.

<sup>&</sup>lt;sup>7</sup> Hawaii Exp. Sta. Bull. 26.

that the amounts of  $\rm H_2SO_4$  thus produced would be so enormous as to make it useless, since the demand for the acid is as yet quite limited. It has been suggested, therefore, among many other proposed uses for it, that  $\rm H_2SO_4$  be used in small quantities in the irrigation water to act as a solvent for soil minerals. It was this idea which suggested the preliminary experiment described below, along with the others, on the effects of the metallic salts on plant growth.

### **Experiments**

The soil employed in the experiments was a light sand with a good humus supply, and was constituted chemically as follows:

Insoluble residue75.77 per cent	$\mathrm{Mn_3O_4}\ldots\ldots$ o.or per cent
Soluble silica 2.94	$P_2O_5$ 0.26
$Fe_2O_3$ 2.05	MgO 0.36
$Al_2O_338$	Na <sub>2</sub> O
CaO 1.59	K <sub>2</sub> O 0.45
$SO_3 \dots \dots$	Humus 2.35

Large 8-inch flower pots were filled with 12 lbs. of soil and treated with varying amounts of the solution of the salt to be tested, each cc. representing a known weight of the salt. The concentrations employed are noted in the tables in parts per million of water free soil. The plants tested were the vetch (Vicia sativa) and the Little Club variety of wheat. Eight seeds, which were carefully selected, were planted in each pot, and after some growth was made were thinned to 4 plants per pot. The pots were carefully irrigated so as to give the soil an optimum moisture content but not allow any moisture to percolate from the soil, thus preventing loss of the salts tested. The plants were all grown under glass and appeared to make good vigorous growth from the start. appearance of the aphis and other insects in large numbers undoubtedly had something to do with diminishing the total yield of dry matter, but not enough to affect the results seriously. was not allowed to mature, but had to be harvested about the same time that the wheat was cut, because the mildew had attacked the plants rather seriously. The wheat was mature, however, when harvested. In the case of the vetch, the weight of the tops, as well as that of the roots, is given, while in the case of the wheat, only the

weight of the tops as dry matter is recorded. The following tables give all other explanatory data and results of the experiments, and a discussion follows each table.

	$\mathbf{T}$	ABLE	Ι	
EFFECTS	OF	CuSO <sub>4</sub>	ON	PLANTS

CuSO <sub>4</sub> ppm.	Dry weigh	T OF VETCH	DRY WEIGHT OF WHEAT
	Roots gm.	Tops gm.	Tops gm.
0	4.5	12.0	18.5
5	1.8	20.5	15.7
10	5 - 5	20.0	16.2
20	4.0	21.0	17.5
40	5 · 5	17.5	13.0
100	3.0	18.0	16.5
200	4.5	14.0	17.2
400	Det. lost	12.0	19.0
600			12.7
1000	1.5	13.0	. 9.7

To one accustomed to regard CuSO<sub>4</sub> as an extremely poisonous salt for plants, the data in table I offer a surprise. While it is true that in the case of the wheat no stimulation from CuSO<sub>4</sub> is evident, its toxic nature likewise cannot be said to manifest itself until a concentration of 1000 ppm. is reached, if then. The last phrase is used advisedly, since the plants in the 600 and 1000 ppm. concentrations of CuSO<sub>4</sub> were started three weeks later than the rest. Germination of the wheat seeds seemed to proceed with much greater rapidity in the higher concentrations, but the plants though growing fast did not seem to possess the deep green color which is so characteristic of plants well nourished. These plants, however, matured at about the same time as the other wheat plants growing in the lower concentrations of CuSO<sub>4</sub>, and produced normal heads.

In the case of the vetch plants, there seems to have been a stimulation due to CuSO<sub>4</sub>, and then what might perhaps be looked upon as toxicity in the highest concentrations. It should be noted, however, that here, as in the case of the wheat, the vetch plants growing in the higher concentrations of copper were planted three weeks later than those growing in the soils with lower concentrations

of copper. It is especially interesting here to mention the rapid and rank growth made by the vetch plants in the highest concentration of copper. All the seeds germinated and the vetch plants seemed to grow erect to a height of 6 inches or more before they began to bend downward by their own weight. The plants in the normal soil and in those with low concentrations of copper made but very little upright growth. One further point is of great interest in regard to the vetch plants, and that is that even at the highest concentrations of copper, the root development appeared to be normal and showed a marked and vigorous development of nodules (the soils were all inoculated). In general the effects of the copper sulphate as given in table I stand out in sharp contrast with the results above reviewed. They exhibit, on the one hand, a very much greater resistance to the effects of copper on the part of both wheat and the vetch plants than HAYWOOD observed in the case of wheat and rye as above noted; and on the other hand, our observations on the plants growing in the highest concentrations of copper given in table I lead us to believe that they will not withstand amounts of copper at all to be compared with those tolerated by the plants with which the experiments at the New York Experiment Station were carried out. From our results it would appear that the use of irrigation water containing a few parts of copper per million would not for many years react deleteriously to plant growth, while the very reverse is believed by HAYWOOD on the basis of his results. Further results were promised by HAYWOOD in 1908 based on his experiments with soils, but none have as yet appeared.

With reference to the cause of the injurious action of copper there are two explanations. One shows that there is direct injury due to absorption of copper as manifested by analysis, and frequently showing a large quantity of copper in plants sprayed with fungicides or in those growing in soils with a high copper content. Haselhoff, however, whose work is cited above, claims that his investigations indicate an increased solution of lime and potash and subsequent leaching away of these materials through the action of copper sulphate, and that injury can be averted by applications of CaCO<sub>3</sub> to replace the losses taking place as indicated.

The next series deals with the effects of ZnSO<sub>4</sub> on plants. The experiment was arranged similarly to the preceding, but the concentrations are slightly different, as shown in table II.

ZnSO <sub>4</sub> ppm.	DRY WEIGHT OF VETCH		DRY WEIGHT OF WHEAT
	Roots gm.	Tops gm.	Tops gm.
0	4.5	12.0	18.5
10	1.5	12.5	17.5
20	3.0	20.0	18.5
100	$4 \cdot 5$	22.0	18.5
200	4.5	20.0	14.6
300	2.0	20.0	10.8
400	1.8	18.0	19.8
500	1.5	15.5	13.7

These results do not show any marked toxicity of ZnSO<sub>4</sub> either for the vetch or the wheat. In the case of the vetch, there would even seem to be an appreciable degree of stimulation up to rather large concentrations of zinc. We can certainly not confirm any toxic effects of zinc salts on plants observed by others, at any rate so far as the concentrations employed above are concerned. seeds germinated in the zinc-treated soils in a normal manner, and the plants in all the concentrations of the ZnSO<sub>4</sub> seemed to make a normal growth. Whatever differences may be noted in table II between the growths made in the pots of the different concentrations of salt employed must be attributed to insect or fungus injury rather than to any effect of the ZnSO<sub>4</sub>. A comparison of our results with the effects of zinc noted by Ehrenberg, whose work is above cited, would seem to indicate that the later investigations8 attribute both favorable and unfavorable effects to the zinc dissolved out from the galvanized iron cylinders used in the vegetation experiments. EHRENBERG claims that zinc acts favorably in that it displaces the bases from their insoluble combinations, and because of its harmful effect on soil organisms makes less competition for the plant in the latter's search for soil nitrogen. On the other hand, the same author points out that zinc sets free hydroxyl ions which exercise

<sup>8</sup> Landw. Versuchs. 72:15. 1910.

a corrosive effect on plants, and that a too rapid displacement of bases in the soil and their subsequent leaching tends to cause soil acidity.

It is to be regretted that Ehrenberg's researches were carried out from the point of view merely of establishing the feasibility of employing vegetation cylinders containing zinc, and therefore we have nothing to guide us to the extent of the solution of zinc and the toxic limit thereof. It appears to us, further, that it is begging the question to assert that the toxic effect of zinc on soil organisms is of benefit to plants for the reason mentioned, because we have no definite data concerning the effects of zinc on soil bacteria or other soil organisms, and certainly not evidence enough, so far, to point to wide differences between the effects of zinc on the higher plants and soil bacteria. From the data in table II, at any rate. it would appear that plants will tolerate and will not be affected by even very considerable quantities of zinc. In connection with this series of experiments in particular, it is desirable to have more experimental data, which we are attempting to secure in further experiments now under way.

The numerous and conflicting results obtained by different investigators in the study of the physiological effects of manganese salts on plants made it desirable to work further with these interesting compounds, and an experiment was arranged, therefore, in which this problem could be studied. The arrangement of the experiment with the results obtained are given in table III.

TABLE III

EFFECTS OF MNSO<sub>4</sub> ON PLANTS

MnSO <sub>4</sub> ppm.	DRY WEIGHT OF VETCH		DRY WEIGHT OF WHEAT
	Roots gm.	Tops gm.	Tops gm.
0	4.5	12.0	18.5
20	4.0	9.5	16.2
40	3.5	11.5	20.0
80	6.0	15.0	21.5
200	4.0	18.0	25.I
400	5.0	17.5	23.2
800	5 · 5	19.5	26.0
2000	3.5	10.0	32.5

It is clear from the data given in table III that both wheat and vetch are stimulated by the presence in the soil of MnSO<sub>4</sub> until the concentration of the latter there reaches an equivalent of 2000 ppm. for the wheat, and 800 ppm. for the vetch. Indeed, the total yields of dry matter obtained from the wheat growing in the pots with the highest concentrations of MnSO<sub>4</sub> surpass quite markedly the yields obtained in any of the pots of the other series described in this paper, and which were planted contemporaneously with the former. In the case of the vetch, the stimulation does not seem to be as great as in the case of the wheat, but from one series of experiments it is difficult to say if stimulation actually stops for the vetch at a concentration of 2000 ppm. of MnSO<sub>4</sub>, since the poor growth obtained there may have been due to experimental error.

These results are an interesting contribution to the subject of the effects of manganese salts on plants. It is not our intention here to discuss the large number of investigations bearing on this subject, especially since this has already been so well done by Kelley, in the work above referred to. In general, however, it would appear from such a review that the largest number of investigations on the subject indicate a stimulating power of manganese sulphate for plants, results with which ours are in accord. There are several cases, however, in which manganese compounds have been observed to depress crop yields, and this point would seem particularly to deserve brief discussion. The experiments dealing with this subject which have thus far been carried out have included tests of many different manganese compounds, and a comparison of the results obtained with different compounds in trying to determine the specific effects of manganese would seem to us to be manifestly unfair. One of us has pointed out elsewhere that the anion as well as the kation of salts must be taken into consideration when the effects of salts on living organisms are studied. such be the case, and we have every reason to believe that it is, then only the experiments bearing on the effects of MnSO<sub>4</sub> on plants should be compared when that subject is studied, and not the effects of the nitrate, chloride, oxide, sulphate, and other compounds. When that is done, it will be found that the percentage of investi-

<sup>9</sup> Centr. Bakt. 33:305.

gations dealing with the subject under discussion in which MnSO<sub>4</sub> has not been found, in relatively small quantities, to act as a stimulant is indeed very small. Obviously when very large concentrations of MnSO<sub>4</sub> are employed it will be found toxic. As investigations of Kelley above referred to have shown, a large variety of plants is affected more or less seriously by the manganese of soils which have shown a content of that material equivalent in some cases to more than 9 per cent of Mn<sub>3</sub>O<sub>4</sub> in the soil. However, such manganiferous soils are limited in extent and, undoubtedly even then, owe their unfavorable nature, in part, to the form of the manganese which they contain. This point appears to us so important as to render a comparison of past results on manganese investigations of little value when it is not considered. It would seem from our results in this series of experiments, and others of a similar nature which they help to confirm, that distinct increases in crop yields of certain plants may be induced by employing MnSO<sub>4</sub> in small quantities as a soil amendment. The manganese content of most "normal" soils is very small, and therefore the dangers arising from the presence of large amounts of manganese, as Kelley has observed them on certain Hawaiian soils, are certainly very remote ones when considered in relation to these normal soils. Small additions of manganese should increase yields, therefore, without introducing dangers. We hope to report further results on this subject later.

As was pointed out above, it has been suggested by some chemists, among the many other uses proposed for H<sub>2</sub>SO<sub>4</sub> when it is produced in enormous quantities from the SO<sub>2</sub> of the smelter fumes, that it could be employed in small quantities in the irrigation water, and, through the solution of mineral plant foods in the soil, be a considerable aid to the nutrition of plants directly, besides exerting perhaps a very marked influence indirectly on soil fertility as will be discussed later. In connection with soils containing black alkali, sulphuric acid would have an added value, if it were satisfactory in other ways, in that it would change the black to the white alkali more cheaply than gypsum does, and it could be applied more easily with irrigation water. Indeed, it is possible that in soils with a content of Na<sub>2</sub>CO<sub>3</sub>, not too large, the sulphuric

<sup>10</sup> Soils ordinarily cropped.

acid treatment of soil may prove a valuable practice. The following experiment was considered, therefore, of very great interest as a preliminary test of the physiological effect of H<sub>2</sub>SO<sub>4</sub> on plants, and its arrangement and results are set forth in table IV.

H <sub>4</sub> SO <sub>4</sub> ppm.	DRY WEIGHT OF VETCH		DRY WEIGHT OF WHEAT
	Roots gm.	Tops gm.	Tops gm.
0	4.5	12.0	18.50
50	5 · 5	15.0	12.20
100	6.0	15.5	16.65
200	3.5	8.0	18.50
300	4.0	19.5	20.50
400	4.0	17.0	10.50
600	5.0	15.5	26.20

The foregoing data would seem to indicate that considerable amounts of H<sub>2</sub>SO<sub>4</sub> may be added to soils without injury to plants. The objection, of course, to which such additions of acid would be open to in practice, is that when the lime and other bases have been neutralized in the soil by the acid, any further additions to the latter would tend to make an acid soil which is unfavorable for plant growth, but it is at any rate safe to assume that on strongly alkaline soils, where that condition is the interfering fact with plant growth, the acid treatment of soil should ameliorate its unfavorable condition to a marked degree. Moreover, we are not without Symmonds<sup>11</sup> has shown that a basis in fact for our assumption. when nitric acid to the extent of 600 pounds per acre was mixed with artesian water and applied to soils containing alkali, the yields of crops were greatly increased. It may be argued, of course, that this case is not an analogous one, since the nitric acid combines with bases in the soil to form nitrates which are an important food and even stimulant to plant growth, but it should also be remembered that, as one of us has already pointed out elsewhere, in a publication above cited, on the basis of direct investigations, that Na<sub>2</sub>SO<sub>4</sub>, produced through the action of H<sub>2</sub>SO<sub>4</sub> on Na<sub>2</sub>CO<sub>3</sub> (black alkali), is a stimulant to nitrification, and that thus an application of

<sup>11</sup> Agric. Gaz. N.S. Wales 21:257-266.

H<sub>2</sub>SO<sub>4</sub> to soils would render a service to the plant different in degree only but not in kind from that rendered by the application of HNO<sub>3</sub>.

#### General remarks

While we offer the results given above as a preliminary report merely, on a series of investigations which we trust will ultimately make a thorough survey of the subject, we must conclude from these data that the tolerance of plants for certain of the inorganic salts, commonly regarded as very poisonous, is much greater than we have been wont to believe. It is true that we have commonly accepted the idea that very small quantities of poisons may act as stimulants, but our results show that plants do not merely tolerate but are actually stimulated by quite considerable quantities of these toxic salts. It is very desirable, therefore, to arrive at a definite understanding of the limits of toxicity of the substances in question, which we are now endeavoring to do.

It would appear to us, further, that the results we have obtained are sufficient evidence to prove that a more thorough investigation into the effects of smelter wastes on plants is necessary before we are enabled to determine justly whether from that standpoint smelter plants are inflicting appreciable injury on the soils immediately surrounding them and on the soils of contiguous territory.

Our results on the effects of MnSO<sub>4</sub> are considered of importance here both because of the stimulating effect of the former on plants and the attempts which have been made to make use of that fact in the employment of manganese salts as fertilizers. Moreover, our data form another link in the chain of evidence which show the stimulating effects of manganese sulphate on plants.

It may not be amiss to add here, also, that to make these investigations more complete we have been making studies of the bacterial flora in the soils employed in the experiments above described. From these we have already obtained data of great interest, which seem to indicate that the soil flora is permanently modified by the treatment of the soil outlined above. The publication of these results is reserved for another paper.

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